IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re United States Patent Application of:

Applicant: **Van Buskirk et al.**

Serial No.: **New Continuation of Prior Copending U.S. Patent Application No. 09/251,890**

Date Filed: **July 12, 2001**

Title: **Scalable lead Zirconium Titanate (PZT) Thin Film Material and Deposition Method, and Ferroelectric Memory Device Structures Comprising Such Thin Film Material High Density Ferroelectric Memory Device Structures**

Docket No.: ATMI-0357 DIV

Examiner: James Park

Art Unit: 2811

EXPRESS MAIL CERTIFICATE

I hereby certify that I am mailing the attached documents to the Commissioner for Patents on the date specified, in an envelope addressed to the Commissioner for Patents, Box AF, Washington, DC 20231, and Express Mailed under the provisions of 37 CFR 1.10.

Lee Ann DiLello

Lee Ann DiLello

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PRELIMINARY AMENDMENT OF NEW CONTINUATION OF PRIOR COPENDING U.S. PATENT APPLICATION NO. 09/251,890

Box AF
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Sir:

Prior to examining the instant application on the merits, please amend the specification as follows:

IN THE SPECIFICATION

Please amend the specification by inserting before the first line the sentence --This is a continuation of U.S. Application No. **09/251,890**, now pending.--

IN THE CLAIMS

1.-37. Canceled.

38. A method of fabricating a ferroelectric PZT film on a substrate, comprising forming the film by liquid delivery MOCVD on the substrate under MOCVD conditions producing a ferroelectric PZT material **having at least one scalable character selected from the group consisting of dimensionally scalable character, pulse length scalable character and E-field scalable character, and wherein said PZT material has at least one of property selected from the group consisting of having a thickness from about 20 to about 150 nanometers, having a ferroelectric operating voltage below 2 Volts, having at least one Type 1 properties and having at least one Type 2 properties**. **[according to any one of claims 1 to 29].**

56. A method of fabricating a ferroelectric PZT film on a substrate, comprising forming the film by liquid delivery MOCVD on the substrate under MOCVD conditions including nucleation conditions producing a ferroelectric PZT material **having at least one scalable character selected from the group consisting of dimensionally scalable character, pulse length scalable character and E-field scalable character, and wherein said PZT material has at least one of**

property selected from the group consisting of having a thickness from about 20 to about 150 nanometers, having a ferroelectric operating voltage below 2 Volts, having at least one Type 1 properties and having at least one Type 2 properties. [according to any one of claims 1 to 29.]

57. A method of fabricating a ferroelectric PZT film on a substrate, comprising forming the film by liquid delivery MOCVD on the substrate under MOCVD conditions including temperature, pressure and liquid precursor solution A/B ratio determined by plateau effect determination from a correlative empirical matrix of plots of each of ferroelectric polarization, leakage current density and atomic percent lead in PZT films, as a function of each of temperature, pressure and liquid precursor solution A/B ratio, wherein A/B ratio is the ratio of Pb to (Zr + Ti), and wherein said ferroelectric PZT film comprises a ferroelectric PZT material **having at least one scalable character selected from the group consisting of dimensionally scalable character, pulse length scalable character and E-field scalable character, and wherein said PZT material has at least one of property selected from the group consisting of having a thickness from about 20 to about 150 nanometers, having a ferroelectric operating voltage below 2 Volts, having at least one Type 1 properties and having at least one Type 2 properties. [according to any one of claims 1 to 29.]**

60. A method of fabricating a FeRAM device, comprising forming a capacitor on a substrate including a ferroelectric PZT material **having at least one scalable character selected from the group consisting of dimensionally scalable character, pulse length scalable character and E-field scalable character, and wherein said PZT material has at least one of property selected from the group consisting of having a thickness from about 20 to about 150 nanometers, having a ferroelectric operating voltage below 2 Volts, having at least one**

Type 1 properties and having at least one Type 2 properties, **[according to any one of claims 1 to 29]** wherein the ferroelectric PZT material is deposited by liquid delivery MOCVD under MOCVD conditions yielding said ferroelectric PZT material.

61. Canceled.

CONCLUSION

Applicants have now made an earnest attempt to place this case in condition for allowance. For the foregoing reasons and for other reasons clearly apparent, Applicants respectfully request examination and consideration of this Application and full allowance of Claims 38-60 and 62-64.

The Commissioner is hereby authorized to charge any fees or credit any overpayments to Deposit Account No. 50-0860 of Advanced Technology Materials, Inc.

Respectfully submitted,

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APPENDIX A
Version with Markings to Show Changes Made

What is claimed is:

1.-37. Canceled.

38. A method of fabricating a ferroelectric PZT film on a substrate, comprising forming the film by liquid delivery MOCVD on the substrate under MOCVD conditions producing a ferroelectric PZT material **having at least one scalable character selected from the group consisting of dimensionally scalable character, pulse length scalable character and E-field scalable character, and wherein said PZT material has at least one of property selected from the group consisting of having a thickness from about 20 to about 150 nanometers, having a ferroelectric operating voltage below 2 Volts, having at least one Type 1 properties and having at least one Type 2 properties. [according to any one of claims 1 to 29].**

39. The method of claim 38, wherein the MOCVD conditions include use of a lead source reagent selected from the group consisting of $Pb(thd)_2$ and $Pb(thd)_2pmdeta$.

40. The method of claim 38, wherein the MOCVD conditions include use of a zirconium source reagent selected from the group consisting of $Zr(thd)_4$ and $Zr(O\text{-}i\text{-}Pr)_2(thd)_2$.

41. The method of claim 38, wherein the MOCVD conditions include use of $Ti(O\text{-}i\text{-}Pr)_2(thd)_2$ as a titanium source reagent.

42. The method of claim 38, wherein the MOCVD conditions include use of $Pb(thd)_2$, Ti(O-i-

$Pr)_2(thd)_2$ and $Zr(thd)_4$ as respective lead, titanium and zirconium source reagents.

43. The method of claim 38, wherein the MOCVD conditions include use of $Pb(thd)_2pmdeta$, $Ti(O\text{-}i\text{-}Pr)_2(thd)_2$ and $Zr(thd)_4$ as respective lead, titanium and zirconium source reagents.

44. The method of claim 38, wherein the MOCVD conditions include use of $Pb(thd)_2pmdeta$, $Ti(O\text{-}i\text{-}Pr)_2(thd)_2$ and $Zr(O\text{-}i\text{-}Pr)_2(thd)_2$ as respective lead, titanium and zirconium source reagents.

45. The method of claim 38, wherein the source reagents are provided for liquid delivery MOCVD in a solvent medium comprising one or more solvent species selected from the group consisting of: tetrahydrofuran, glyme solvents, alcohols, hydrocarbon solvents, hydroaryl solvents, amines, polyamines, and mixtures of two or more of the foregoing.

46. The method of claim 38, wherein the source reagents are provided for liquid delivery MOCVD in a solvent medium comprising tetrahydrofuran: isopropanol: tetraglyme in an 8:2:1 volume ratio.

47. The method of claim 38, wherein the source reagents are provided for liquid delivery MOCVD in a solvent medium comprising octane: decane: polyamine in a 5:4:1 volume ratio.

48. The method of claim 38, wherein the source reagents are provided for liquid delivery MOCVD in a solvent medium comprising octane: polyamine in a 9:1 volume ratio.

49. The method of claim 38, wherein the source reagents are provided for liquid delivery MOCVD in a solvent medium comprising tetrahydrofuran.

50. The method of claim 38, wherein the substrate comprises a noble metal.

51. The method of claim 38, wherein the substrate comprises a noble metal selected from the group consisting of iridium, platinum, and combinations thereof.

52. The method of claim 38, wherein the substrate comprises a TiAlN barrier layer overlaid by an iridium layer.

53. The method of claim 38, wherein the liquid delivery MOCVD includes vaporization of a source reagent solution to form precursor vapor therefrom and flowing the precursor vapor to a CVD chamber in a carrier gas.

54. The method of claim 53, wherein the carrier gas is selected from the group consisting of argon, helium and mixtures thereof.

55. The method according to claim 38, further comprising flowing to the CVD chamber an oxidant medium including at least one species selected from the group consisting of O_2, O_3, N_2O, and O_2/N_2O.

56. A method of fabricating a ferroelectric PZT film on a substrate, comprising forming the film by liquid delivery MOCVD on the substrate under MOCVD conditions including nucleation conditions producing a ferroelectric PZT material <u>**having at least one scalable character selected from the group consisting of dimensionally scalable character, pulse length scalable character and E-field scalable character, and wherein said PZT material has at least one of property selected from the group consisting of having a thickness from about 20 to about**</u>

150 nanometers, having a ferroelectric operating voltage below 2 Volts, having at least one Type 1 properties and having at least one Type 2 properties. [according to any one of claims 1 to 29.]

57. A method of fabricating a ferroelectric PZT film on a substrate, comprising forming the film by liquid delivery MOCVD on the substrate under MOCVD conditions including temperature, pressure and liquid precursor solution A/B ratio determined by plateau effect determination from a correlative empirical matrix of plots of each of ferroelectric polarization, leakage current density and atomic percent lead in PZT films, as a function of each of temperature, pressure and liquid precursor solution A/B ratio, wherein A/B ratio is the ratio of Pb to (Zr + Ti).

58. A method of fabricating a ferroelectric PZT film on a substrate, comprising forming the film by liquid delivery MOCVD on the substrate under MOCVD conditions including temperature, pressure and liquid precursor solution A/B ratio determined by plateau effect determination from a correlative empirical matrix of plots of each of ferroelectric polarization, leakage current density and atomic percent lead in PZT films, as a function of each of temperature, pressure and liquid precursor solution A/B ratio, wherein A/B ratio is the ratio of Pb to (Zr + Ti), and wherein said ferroelectric PZT film comprises a ferroelectric PZT material **having at least one scalable character selected from the group consisting of dimensionally scalable character, pulse length scalable character and E-field scalable character, and wherein said PZT material has at least one of property selected from the group consisting of having a thickness from about 20 to about 150 nanometers, having a ferroelectric operating voltage below 2 Volts, having at least one Type 1 properties and having at least one Type 2 properties. [according to any one of claims 1 to 29.]**

59. A method of fabricating a ferroelectric PZT film on a substrate, comprising forming the film by liquid delivery MOCVD on the substrate under MOCVD conditions including Correlative Materials or Processing Requirements, to yield a ferroelectric PZT film having PZT Properties, wherein said Correlative Materials or Processing Requirements and PZT Properties comprise:

PZT Properties	**Correlative Materials or Processing Requirements**
Basic properties:	
Ferroelectric polarization $P_{sw} > 20\ \mu C/cm^2$	Film Pb concentration > threshold level; operation on A/B plateau above the knee region, and with temperature, pressure and gas phase A/B concentration ratio defined by plateau effect determination
Leakage current density $J < 10^{-5}\ A/cm^2$ at operating voltage	Film Pb concentration within a range (between the minimum and maximum) on the A/B plateau, and with temperature, pressure and gas phase A/B concentration ratio defined by plateau effect determination
Dielectric relaxation For characteristic J^{-n} □log (time), $n > 0.5$ and $J < 1\%$ ferroelectric switching current from 0-100 ns.	Zr/Ti ratio < 45/55 Deposition P > 1.8 torr
Retention Maintenance of ferroelectric properties (ferroelectric domains)	Operation within ranges of temperature, pressure and gas phase A/B concentration ratio defined by plateau effect determination
Avoidance of cycling fatigue $P_{sw} < 10\%$ decrease after 10^{10} cycles	Use of Ir-based electrodes
E-field scalability	Operation within ranges of temperature, pressure and gas phase A/B concentration ratio defined by plateau effect determination

Surface smoothness	Nucleation-growth conditions during film formation within ranges of temperature, pressure and gas phase A/B concentration ratio defined by plateau effect determination
Grain size	Nucleation-growth conditions during film formation within ranges of temperature, pressure and gas phase A/B concentration ratio defined by plateau effect determination

60. A method of fabricating a FeRAM device, comprising forming a capacitor on a substrate including a ferroelectric PZT material **having at least one scalable character selected from the group consisting of dimensionally scalable character, pulse length scalable character and E-field scalable character, and wherein said PZT material has at least one of property selected from the group consisting of having a thickness from about 20 to about 150 nanometers, having a ferroelectric operating voltage below 2 Volts, having at least one Type 1 properties and having at least one Type 2 properties,** **[according to any one of claims 1 to 29]** wherein the ferroelectric PZT material is deposited by liquid delivery MOCVD under MOCVD conditions yielding said ferroelectric PZT material.

61. **Canceled.**

62. The method of claim 60, wherein the PZT film defines a capacitor area of from about 10^4 to about 10^{-2} □m^2.

63. The method of claim 60, wherein the MOCVD conditions are determined by plateau effect

determination.

64. The method of claim 60, wherein the MOCVD conditions comprise Correlative Materials or Processing Requirements, to yield a ferroelectric PZT film having PZT Properties, wherein said Correlative Materials or Processing Requirements and PZT Properties comprise:

PZT Properties	**Correlative Materials or Processing Requirements**
Basic properties:	
Ferroelectric polarization $P_{sw} > 20\ \mu C/cm^2$	Film Pb concentration > threshold level; operation on A/B plateau above the knee region, and with temperature, pressure and gas phase A/B concentration ratio defined by plateau effect determination
Leakage current density $J < 10^{-5}\ A/cm^2$ at operating voltage	Film Pb concentration within a range (between the minimum and maximum) on the A/B plateau, and with temperature, pressure and gas phase A/B concentration ratio defined by plateau effect determination
Dielectric relaxation For characteristic J^{-n} □log (time), $n > 0.5$ and $J < 1\%$ ferroelectric switching current from 0-100 ns.	Zr/Ti ratio < 45/55 Deposition P > 1.8 torr
Retention Maintenance of ferroelectric properties (ferroelectric domains)	Operation within ranges of temperature, pressure and gas phase A/B concentration ratio defined by plateau effect determination
Avoidance of cycling fatigue $P_{sw} < 10\%$ decrease after 10^{10} cycles	Use of Ir-based electrodes
E-field scalability	Operation within ranges of temperature, pressure and gas phase A/B concentration ratio

	defined by plateau effect determination
Surface smoothness	Nucleation-growth conditions during film formation within ranges of temperature, pressure and gas phase A/B concentration ratio defined by plateau effect determination
Grain size	Nucleation-growth conditions during film formation within ranges of temperature, pressure and gas phase A/B concentration ratio defined by plateau effect determination

APPENDIX B
Clean Copy of All Pending Claims

What is claimed is:

1.-37. Canceled.

38. A method of fabricating a ferroelectric PZT film on a substrate, comprising forming the film by liquid delivery MOCVD on the substrate under MOCVD conditions producing a ferroelectric PZT material having at least one scalable character selected from the group consisting of dimensionally scalable character, pulse length scalable character and E-field scalable character, and wherein said PZT material has at least one of property selected from the group consisting of having a thickness from about 20 to about 150 nanometers, having a ferroelectric operating voltage below 2 Volts, having at least one Type 1 properties and having at least one Type 2 properties.

39. The method of claim 38, wherein the MOCVD conditions include use of a lead source reagent selected from the group consisting of $Pb(thd)_2$ and $Pb(thd)_2pmdeta$.

40. The method of claim 38, wherein the MOCVD conditions include use of a zirconium source reagent selected from the group consisting of $Zr(thd)_4$ and $Zr(O\text{-}i\text{-}Pr)_2(thd)_2$.

41. The method of claim 38, wherein the MOCVD conditions include use of $Ti(O\text{-}i\text{-}Pr)_2(thd)_2$ as a titanium source reagent.

42. The method of claim 38, wherein the MOCVD conditions include use of $Pb(thd)_2$, $Ti(O\text{-}i\text{-}Pr)_2(thd)_2$ and $Zr(thd)_4$ as respective lead, titanium and zirconium source reagents.

43. The method of claim 38, wherein the MOCVD conditions include use of $Pb(thd)_2pmdeta$, $Ti(O\text{-}i\text{-}Pr)_2(thd)_2$ and $Zr(thd)_4$ as respective lead, titanium and zirconium source reagents.

44. The method of claim 38, wherein the MOCVD conditions include use of $Pb(thd)_2pmdeta$, $Ti(O\text{-}i\text{-}Pr)_2(thd)_2$ and $Zr(O\text{-}i\text{-}Pr)_2(thd)_2$ as respective lead, titanium and zirconium source reagents.

45. The method of claim 38, wherein the source reagents are provided for liquid delivery MOCVD in a solvent medium comprising one or more solvent species selected from the group consisting of: tetrahydrofuran, glyme solvents, alcohols, hydrocarbon solvents, hydroaryl solvents, amines, polyamines, and mixtures of two or more of the foregoing.

46. The method of claim 38, wherein the source reagents are provided for liquid delivery MOCVD in a solvent medium comprising tetrahydrofuran: isopropanol: tetraglyme in an 8:2:1 volume ratio.

47. The method of claim 38, wherein the source reagents are provided for liquid delivery MOCVD in a solvent medium comprising octane: decane: polyamine in a 5:4:1 volume ratio.

48. The method of claim 38, wherein the source reagents are provided for liquid delivery MOCVD in a solvent medium comprising octane: polyamine in a 9:1 volume ratio.

49. The method of claim 38, wherein the source reagents are provided for liquid delivery MOCVD in a solvent medium comprising tetrahydrofuran.

50. The method of claim 38, wherein the substrate comprises a noble metal.

51. The method of claim 38, wherein the substrate comprises a noble metal selected from the group consisting of iridium, platinum, and combinations thereof.

52. The method of claim 38, wherein the substrate comprises a TiAlN barrier layer overlaid by an iridium layer.

53. The method of claim 38, wherein the liquid delivery MOCVD includes vaporization of a source reagent solution to form precursor vapor therefrom and flowing the precursor vapor to a CVD chamber in a carrier gas.

54. The method of claim 53, wherein the carrier gas is selected from the group consisting of argon, helium and mixtures thereof.

55. The method according to claim 38, further comprising flowing to the CVD chamber an oxidant medium including at least one species selected from the group consisting of O_2, O_3, N_2O, and O_2/N_2O.

56. A method of fabricating a ferroelectric PZT film on a substrate, comprising forming the film by liquid delivery MOCVD on the substrate under MOCVD conditions including nucleation conditions producing a ferroelectric PZT material having at least one scalable character selected from the group consisting of dimensionally scalable character, pulse length scalable character and E-field scalable character, and wherein said PZT material has at least one of property selected from the group consisting of having a thickness from about 20 to about 150 nanometers, having a ferroelectric operating voltage below 2 Volts, having at least one Type 1 properties and having at

least one Type 2 properties.

57. A method of fabricating a ferroelectric PZT film on a substrate, comprising forming the film by liquid delivery MOCVD on the substrate under MOCVD conditions including temperature, pressure and liquid precursor solution A/B ratio determined by plateau effect determination from a correlative empirical matrix of plots of each of ferroelectric polarization, leakage current density and atomic percent lead in PZT films, as a function of each of temperature, pressure and liquid precursor solution A/B ratio, wherein A/B ratio is the ratio of Pb to (Zr + Ti).

58. A method of fabricating a ferroelectric PZT film on a substrate, comprising forming the film by liquid delivery MOCVD on the substrate under MOCVD conditions including temperature, pressure and liquid precursor solution A/B ratio determined by plateau effect determination from a correlative empirical matrix of plots of each of ferroelectric polarization, leakage current density and atomic percent lead in PZT films, as a function of each of temperature, pressure and liquid precursor solution A/B ratio, wherein A/B ratio is the ratio of Pb to (Zr + Ti), and wherein said ferroelectric PZT film comprises a ferroelectric PZT material having at least one scalable character selected from the group consisting of dimensionally scalable character, pulse length scalable character and E-field scalable character, and wherein said PZT material has at least one of property selected from the group consisting of having a thickness from about 20 to about 150 nanometers, having a ferroelectric operating voltage below 2 Volts, having at least one Type 1 properties and having at least one Type 2 properties.

59. A method of fabricating a ferroelectric PZT film on a substrate, comprising forming the film by liquid delivery MOCVD on the substrate under MOCVD conditions including Correlative Materials or Processing Requirements, to yield a ferroelectric PZT film having PZT Properties,

wherein said Correlative Materials or Processing Requirements and PZT Properties comprise:

PZT Properties	**Correlative Materials or Processing Requirements**
Basic properties:	
Ferroelectric polarization $P_{sw} > 20\ \mu C/cm^2$	Film Pb concentration > threshold level; operation on A/B plateau above the knee region, and with temperature, pressure and gas phase A/B concentration ratio defined by plateau effect determination
Leakage current density $J < 10^{-5}\ A/cm^2$ at operating voltage	Film Pb concentration within a range (between the minimum and maximum) on the A/B plateau, and with temperature, pressure and gas phase A/B concentration ratio defined by plateau effect determination
Dielectric relaxation For characteristic J^{-n} □log (time), $n > 0.5$ and $J < 1\%$ ferroelectric switching current from 0-100 ns.	Zr/Ti ratio < 45/55 Deposition P > 1.8 torr
Retention Maintenance of ferroelectric properties (ferroelectric domains)	Operation within ranges of temperature, pressure and gas phase A/B concentration ratio defined by plateau effect determination
Avoidance of cycling fatigue $P_{sw} < 10\%$ decrease after 10^{10} cycles	Use of Ir-based electrodes
E-field scalability	Operation within ranges of temperature, pressure and gas phase A/B concentration ratio defined by plateau effect determination
Surface smoothness	Nucleation-growth conditions during film formation within ranges of temperature, pressure and gas phase A/B concentration ratio defined by plateau

	effect determination
Grain size	Nucleation-growth conditions during film formation within ranges of temperature, pressure and gas phase A/B concentration ratio defined by plateau effect determination

60. A method of fabricating a FeRAM device, comprising forming a capacitor on a substrate including a ferroelectric PZT material having at least one scalable character selected from the group consisting of dimensionally scalable character, pulse length scalable character and E-field scalable character, and wherein said PZT material has at least one of property selected from the group consisting of having a thickness from about 20 to about 150 nanometers, having a ferroelectric operating voltage below 2 Volts, having at least one Type 1 properties and having at least one Type 2 properties, wherein the ferroelectric PZT material is deposited by liquid delivery MOCVD under MOCVD conditions yielding said ferroelectric PZT material.

61. **Canceled.**

62. The method of claim 60, wherein the PZT film defines a capacitor area of from about 10^{4} to about 10^{-2} □m^2.

63. The method of claim 60, wherein the MOCVD conditions are determined by plateau effect determination.

64. The method of claim 60, wherein the MOCVD conditions comprise Correlative Materials or Processing Requirements, to yield a ferroelectric PZT film having PZT Properties, wherein said

Correlative Materials or Processing Requirements and PZT Properties comprise:

PZT Properties	**Correlative Materials or Processing Requirements**
Basic properties:	
Ferroelectric polarization $P_{sw} > 20\ \mu C/cm^2$	Film Pb concentration > threshold level; operation on A/B plateau above the knee region, and with temperature, pressure and gas phase A/B concentration ratio defined by plateau effect determination
Leakage current density $J < 10^{-5}\ A/cm^2$ at operating voltage	Film Pb concentration within a range (between the minimum and maximum) on the A/B plateau, and with temperature, pressure and gas phase A/B concentration ratio defined by plateau effect determination
Dielectric relaxation For characteristic J^{-n} □log (time), $n > 0.5$ and $J < 1\%$ ferroelectric switching current from 0-100 ns.	Zr/Ti ratio < 45/55 Deposition P > 1.8 torr
Retention Maintenance of ferroelectric properties (ferroelectric domains)	Operation within ranges of temperature, pressure and gas phase A/B concentration ratio defined by plateau effect determination
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Grain size	Nucleation-growth conditions during film formation within ranges of temperature, pressure and gas phase A/B concentration ratio defined by plateau effect determination